THE STEREOCHEMISTRY OF INORGANIC COMPLEX COMPOUNDS

I. AN INVESTIGATION OF THE OPTICAL ANOMALY SHOWN BY SOME METAL ORTHO-PHENANTHROLINE COMPLEXES

II. SPECTROGRAPHY AS A METHOD OF STUDYING THE REACTIONS OF COMPLEX METAL AMMINES

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ROBERT CROCKER BRASTED

B.S., George Washington University, 1938

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AN ABSTRACT OF A THESIS

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THE STEREOCHEMISTRY OF INORGANIC COMPLEX COMPOUNDS

I. An Investigation of the Optical Anomaly Shown by Some Metal Ortho-phenanthroline Complexes

II. Spectrography as a Method of Studying the Reactions of Complex Compounds

I. It was noted in 1931 by certain investigators[1] that metal hexaquo bromcamphor-π-sulfonate ($[M(H_2O)_6](BCS)_2$) complexes of the common coordinating divalent metals underwent an anomalous behavior when in the presence of ortho-phenanthroline. The camphor sulfonate and certain alkaloid salts such as strychnine also were affected. When a three molar portion of ortho-phenanthroline was added to the zinc bromcamphor-π-sulfonate salt the rotation of the complex due to the active BCS^- was greatly exalted. With the addition of strychnine to $[Zn(phen)_3]^{++}$ an abnormal decrease in the rotation of the strychnine was noted. α-α'dipyridyl was not as effective in the anomaly and primary amines were without effect. The effect was attributed to an activation caused by the ortho-phenanthroline on coordination, forming an asymmetric configuration on the zinc complex. The present investigators felt that a more complete study of the whole phenomenon was desirable. The following points were therefore studied:

A. Polarimetric study of the optical rotation of varying mols of the BCS^- and $[Zn(phen)_3]^{++}$ ions.

B. Refractometric study of the solutions made up for (A).

C. Conductivity studies of the pure complexes and related complexes for ionization data.

D. Ultraviolet and near ultraviolet studies on ortho-phenanthroline complexes and related complexes.

E. An extension of the study to a trivalent metal complex, namely the triortho-phenanthroline cobaltic ion.

RESULTS: The polarimetric and refractometric studies

show the tendency for a compound formation in the solution when a 2:1 ratio of BCS^- and $[Zn(phen)_3]^{++}$ exists. The same results are found for the strychnine compound. The cobaltic complex (prepared by the addition of stoichiometric quantities of ortho-phenanthroline, cobalt chloride and oxidized by perhydrol in the presence of activated charcoal) was found to behave in the same manner as the divalent metal complexes. The conductivity measurements indicate an incomplete ionization which is contrary to the assumption of the previous investigators. The spectrographic data indicate a definite weighting effect since the maximum of ortho-phenanthroline is shifted to shorter frequencies when the complex with BCS^- is formed. Generally the anion is quite ineffective as far as spectra of the complex are concerned.

CONCLUSIONS: Some type of compound has been formed between the anion and cation (or complex and alkaloid). The forces may well be of the Van derWaals type rather than ionic. The force has caused a distortion in the configuration which is responsible for the optical activity leading to a new activity. The assumption[1] of "activation" does not accord with the experimental data.

II. Initially a study of the reaction between sodium nitrite and the active $[Coen_2Cl(NH_3)]Cl_2$ was desired. The optical rotation of the latter salt is found to decrease rapidly in the presence of nitrite giving finally an inactive product. The intermediate products would be exceedingly hard to isolate and the constitution thus indeterminable especially in view of the fact that most of these intermediates do not differ markedly in color. A spectrographic method for following such reactions was devised by studying the changes in ultraviolet absorption. The modifications involved essentially the elimination of a plate calibration and the judicious use of a Leeds-Northrup Microdensitometer. This enabled one to make as many as fifteen spectrograms on one plate with an hour's time while the period of completing a study including the plots was cut by 70-80 per cent with an untold saving on eye fatigue compared to the use of the Görtner instrument. The relative curves so obtained compare very favorably with true

absorption curves found in the literature. Certain preliminary studies were carried out first on aquotizations while the emphasis on the latter work was on the study of nitrite complex preparations an reactions.

A. A study was made of the aquotization of certain complex aniline derivative-diethylene diamine cobalt complexes previously prepared by L. B. Clapp.[2] These were found to be quite unstable in solution as indicated by an ever increasing transmission in the ultraviolet and the development of a maximum at the wave length typical of the chloro aquo complex.

B. The aquotization of cis and trans $[Coen_2Cl_2]Cl$ was followed spectrographically with time curves.[4] The cis compound was found to aquate more readily as indicated by a shift of the initial maximum toward the higher frequency. The trans was more stable but finally aquated giving a product whose maximum was similar to that of the cis complex.

C. The relationship between the mol ratio of nitrite and trans $[Coen_2Cl_2]Cl$ was studied and the increment of E per mol of nitrite indicated a method of determining the number of NO_2 groups in a complex.

D. The reaction between nitrite and the cis chloro-ammine complex was followed with relation to the changes in optical activity. The maximum typical of chloro nitro compounds increased in E value as the rotation decreased giving a final value at zero rotation typical of cis chloro nitro compounds. This curve is not readily distinguishable from that of the cis dinitro salt since both have almost identical maxima. The maximum for the chloro ammino salt shifts immediately on the addition of nitrite although the change in rotation is very slight. It is possible that the final reaction product is a mixture of cis and trans salts since the location of the maximum is not that of pure cis chloro nitro or dinitro complexes.

E. The preparation of trans $[Coen_2Cl(NH_3)]Cl$ entailed a multistep process[3] involving the formation of a slightly soluble chloro thiocyanato complex which is finally oxidized by perhydrol to the chloro ammine. Practically this synthesis was found to be an extremely uncertain one. Ultraviolet absorption showed that isomerization took place in the purifica-

tion of 1,6[$Coen_2Cl(SCN)$]SCN to form [$Coen_2Cl(NH_3)$]Cl. Further, the crystallization of pure [$Coen_2Cl(NH_3)$]Cl from an alcoholic solution was never attained. The unreacted dithiocyanato complex was the only crystalline product obtained from the reaction mixture. Fresh perhydrol was found to react explosively with the thiocyanato complexes unless precooled to ice bath temperatures and stirred while perhydrol is added dropwise. The preparation of the trans salt was finally accomplished by the treatment of [$Coen_2Cl_2$]Cl (trans) with a methyl alcohol-liquid ammonia solution and the fractional precipitation of the trans chloroammino isomer with dithionate as the last fraction.

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VITA

The author was born August 26, 1915 in Lisbon, North Dakota. His early years were spent in various Army Posts throughout the United States and Philippine Islands; thus his elementary education was received in many locations. His secondary education was received in Englewood, Colorado, and St. Paul, Minnesota. He graduated from the Central High School of the latter city in 1933. He attended the University of Minnesota in the winter of 1933 and the George Washington University from February 1934 until June 1939, receiving the B. A. degree in 1938 and the M. A. degree in 1939. He held undergraduate assistantships in Inorganic and Analytical chemistry in 1937 and 1938 and the Sanders Fellowship in Chemistry in 1939. He entered the University of Illinois in the fall of 1939. He has held an assistantship in Analytical Chemistry since that time. He is a member of Sigma Xi and Phi Lambda Upsilon.

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